

Mean field theory for double-perovskites

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A mean field approximation of a model for double perovskites that takes into account the coupling between itinerant electron spins and localized spins is developed. As in previously reported theoretical results, and contrary to experimental observation, the critical temperature is suppressed for large electron density. An effective Heisenberg model reveals the cause of this discrepancy: the competition between degenerate antiferromagnetic and ferromagnetic channels. This degeneracy can be broken by the inclusion of a Hubbard-type U term. It is therefore suggested that electron correlation effects need to be incorporated in the minimal model of double perovskites in order to explain the experimental observation of increasing ferromagnetic critical temperature with increasing electron doping.

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I. INTRODUCTION

A large magnetoresistance is a desirable property for certain technological applications such as writing and reading magnetic memories. Manganites, the most studied colossal magnetoresistance systems,¹ have the drawback of having low ferromagnetic transition (Curie) temperatures T_C (compared to room temperature). They are half-metals, namely, metallic for one spin orientation and insulating for the other, but this property gets rapidly suppressed when increasing temperature. Half-metallicity produces the low field (extrinsic) magnetoresistance measured in polycrystalline manganites and the tunneling magnetoresistance in artificially created barriers. Increasing the operation temperature of these devices is a major issue that has led to the search of other half-metals with higher T_C . One such example are double perovskites of general formula $A_2BB'O_6$ ($A=\text{Sr,Ca,Ba,Ld,K}$, $B=\text{Fe}$, $B'=\text{Mo,Re}$).^{2,3,4,5} Polycrystalline double perovskites show large magnetoresistance at low fields due to half-metallicity even at room temperature, and their T_C is above 400K.² Band structure calculations^{2,5,6,7,8} reveal a ~ 0.8 eV gap in the majority up spin bands at the Fermi level while the down spin bands cross it.⁶

The ordered double perovskite structure consists of alternating BO_6 and $\text{B}'\text{O}_6$ octahedra in a cubic lattice. Anti-site disorder in this lattice has strong effects in magnetic properties.^{9,10,11,12,13,14} Fe is in the trivalent state ($3d^5$) with its five electrons localized in the spin-up d -orbitals.⁶ Mo^{5+} provides one electron ($4d^1$) per Fe to the conduction band, electron density $c = 1$, and Re^{5+} provides two ($5d^2$), $c = 2$. These electrons are moving in the Fe-Mo/Re hybrid band formed by t_{2g} spin-down orbitals. The cubic symmetry causes a splitting between the t_{2g} and e_g orbitals, such that t_{2g} orbitals are lower in energy and the only ones occupied by the conduction electrons. The spin-down orbitals are well above the spin-up orbitals due to the strong Hund's cou-

pling in Fe (see Fig. 1). Fe is the magnetically active ion; its five localized electrons render a local spin $S = 5/2$. On the other hand, Mo and Re are paramagnetic ions.⁹ The theoretical magnetization per formula unit is $4\mu_B$ though smaller values have been measured probably due to anti-site disorder, as nearest neighbor Fe-Fe superexchange (SE) interaction is antiferromagnetic.^{10,12,13} In an ordered lattice, Fe-Fe SE is very weak as Fe ions are too far away ($> 5.5\text{\AA}$) for this interaction to be important. Doping on the A site changes the density of conduction electrons per Fe: substituting a trivalent ion (e.g. La) for Sr ($\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$) increases the electron density to $c = 1 + x$ while a monovalent ion (e.g. K) gives $c = 1 - x$.

Superexchange interaction, which is extremely weak in double perovskites, has been ruled out as the cause of magnetic ordering in these materials. Instead, there is experimental evidence for the existence of two sublattices,¹⁵ the localized spins in Fe and the delocalized electrons, that interact antiferromagnetically due to the strong Hund's coupling J on Fe ions. Other materials that present these two coupled sublattices are manganites¹ and diluted magnetic semiconductors such as $\text{Ga}_{1-x}\text{Mn}_x\text{As}$.^{16,17} In manganites the conduction electrons are ferromagnetically coupled to the localized Mn spins that form a pseudocubic lattice. Hund's coupling in manganites is very large and, in the limit $J \rightarrow \infty$, leads to the double exchange (DE) mechanism producing ferromagnetism. DE basically implies that the spin of the conduction electron follows the orientation of the local spin. As hopping does not flip the spin, the kinetic energy of the conduction electrons is minimized when the local spins are all parallel to each other.¹⁸ Hund's coupling in double perovskites is antiferromagnetic,¹⁵ as the spin-up Fe levels are fully occupied, but it can equally lead to ferromagnetic order. However, unlike in manganites, the strong Hund's coupling only applies to every other site, since Mo is paramagnetic⁹ and, therefore, the minimal model for double-perovskites is different from the simple DE in manganites.⁶

Susceptibility measurements of double-perovskites in the paramagnetic regime give a positive Curie-Weiss parameter (i.e. ferromagnetic interaction).^{11,15,19} This rules out a superexchange scenario, since SE would only give ferromagnetic Fe ordering through antiferromagnetic coupling between Fe:3d⁵ and Mo:3d¹ (*ferrimagnetic* ordering) and in this case a negative Curie-Weiss parameter should be observed. A conduction electron mediated ferromagnetism is suggested by the observation that the strength of the ferromagnetic coupling and thus, the T_C , can be increased by electron doping.^{13,20,21,22} In turn, the increase in T_C has been shown to be accompanied by an increase of the density of states at the Fermi level.²³

A model for double perovskites that takes into account the coupling between itinerant electrons and localized spins on Fe has previously been studied theoretically by means of dynamical mean-field theory²⁴ and Monte-Carlo simulations.²⁵ Their common result is that the critical temperature T_C is suppressed as the electron density increases above a certain value. This is clearly in contradiction with experimental observations of increasing T_C by electron doping. On the other hand, similar models for perovskite manganites and diluted magnetic semiconductors (GaMnAs) find that the T_C increases with the density of states.

In this paper a mean field theory approximation is developed on this model for ordered double perovskites. The previously published results^{24,25} are recovered in the appropriate limits. As mentioned already, these theoretical results are not consistent with experimental data. The advantage of the mean field theory developed here is that the reason for the failure of this model becomes transparent. The Hamiltonian can be written as an effective Heisenberg model with ferromagnetic and antiferromagnetic terms. Due to the degeneracy of the spin up and down levels in the paramagnetic atom, these two channels compete resulting in the suppression of T_C for large enough values of the electron density. We show how the intraband Coulomb repulsion U , which penalizes the occupation of two spin orientations at the same site, can prefer the FM channel over the AF leading to an increase of T_C with doping, as observed experimentally. This work will not take into account the possibility that the Coulomb repulsion also induces orbital order.²⁶

This paper is organized as follows. In Sec. II the minimal model for double perovskites is introduced. In Sec. III, the mean field approximation is described, the model is written as an effective Heisenberg model, and the effects of adding electron correlation effects are analyzed. In Sec. IV, an alternative mean field calculation is described. This approach integrates out the effect of the paramagnetic sites and considers only the Fe sites, making a clear connection with the double exchange model used in the description of manganites. We conclude in Sec. V.

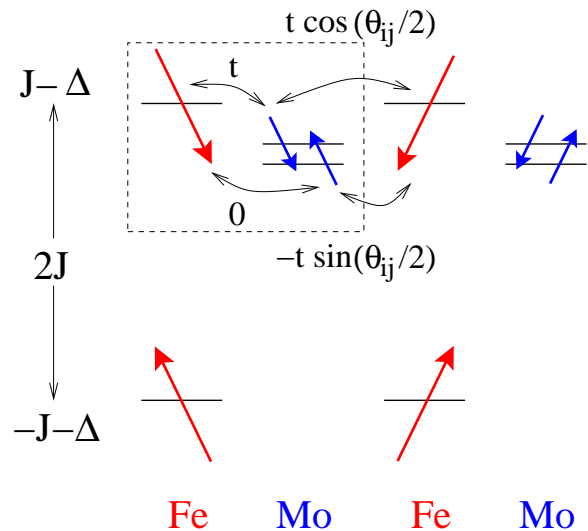


FIG. 1: (color online) Description of the parameters of the model and definition of the paramagnetic state used. t stands for $t_{\text{Fe-Mo}}$. The level with energy $-J - \Delta$ correspond to the localized electrons in $\text{Fe}(3d^5)$ that are considered in the model as localized classical spins $S = 5/2$. The dash box defines the unit cell i . In the limit $J \rightarrow \infty$ the spin of the conduction electron on the upper band is always strictly antiparallel to the localized spin.

II. MODEL

The full Hamiltonian can be written as the sum of two terms

$$H = H_{\text{KE}} + H_{\text{on-site}}. \quad (1)$$

The first term is the kinetic energy of the conduction electrons. The second term takes account of the strong Hund's coupling on Fe sites, J , and the difference in electronegativities, Δ , between Fe and Mo/Re sites.

The conduction electrons move between t_{2g} orbitals. These orbitals have planar symmetry which implies hybridization only takes place between t_{2g} orbitals of the same symmetry. Therefore, the kinetic energy consists of three degenerate, two dimensional, tight binding systems xy , yz , and zx , $H_{\text{KE}} = H_{xy}^{\text{KE}} + H_{yz}^{\text{KE}} + H_{zx}^{\text{KE}}$. The matrix element $t_{\text{Fe-Mo}}$ connects the d_{ab} ($a, b = x, y, z$) orbitals of nearest neighbors in the ab plane. $t_{\text{Mo-Mo}}$ connects nearest neighbors in the Mo sublattice. $t_{\text{Fe-Fe}}$ is expected to be very small due to the more localized nature of the $3d$ states, and is neglected here.

The large local spins on Fe sites ($S = 5/2$) can be considered classical and are characterized by an angle θ_i . Due to the large value for the Hund's coupling, the spin of the conduction electron on Fe follows adiabatically the classical local spin configuration.

III. MEAN FIELD APPROXIMATION. DISPERSIVE MO BANDS.

T_C is calculated from the expansion of the Free Energy F in powers of the magnetization $m = \langle \cos \theta_i \rangle$, which is very small close to T_C . T_C is defined by the condition $\partial^2 F / \partial m^2 = 0$. In order to write the Free Energy, we have to define the paramagnetic regime correctly. Diagonalization of the one-dimensional problem shows that the density of states has a gap in the paramagnetic regime. This gap is related to the fact that Mo is paramagnetic and there are two conducting channels: one through each spin orientation.

In the paramagnetic regime, the spins on the Fe become randomly oriented. Mo is paramagnetic, allowing two spin states. To recover the gap in the DOS, the orientation of these two states in the Mo has to be referenced to a neighboring Fe spin, as shown in Fig. 1. The Fe and

Mo related in this way constitute our unit cell. In this way, the spin of the electrons in the Mo is chosen to be parallel or antiparallel to the direction of the Fe spin in the same cell. Inside the unit cell, the Fe-Mo hopping is 1 (for parallel spins) or 0 (for anti-parallel spins) and between different cells it is determined by the angle formed by Fe ions in neighboring cells $\theta_{ij} = \theta_i - \theta_j$: $\cos(\theta_{ij}/2)$ (spin \uparrow channel) and $\sin(\theta_{ij}/2)$ (spin \downarrow channel). Therefore, the system consists of two different channels that could not be distinguished if the relative orientation of the spins in Mo and Fe were not correctly defined. In the virtual crystal approximation, each site sees an average of all the sites in the lattice so the relevant coefficients of the hopping terms are the thermal averages $\langle \cos(\theta_{ij}/2) \rangle \equiv \langle \cos(\theta/2) \rangle$ and $\langle \sin(\theta_{ij}/2) \rangle \equiv \langle \sin(\theta/2) \rangle$. In the paramagnetic regime both are equal to $2/3$.

For each of the equivalent planes, the Hamiltonian can then be written

$$H_{xy} = (J - \Delta) \sum_i d_i^+ d_i + t_{\text{Mo-Mo}} \sum_{\langle i,j \rangle} \left[\left\langle \cos \frac{\theta}{2} \right\rangle (c_{i,p}^+ c_{j,p} + c_{i,ap}^+ c_{j,ap}) - \left\langle \sin \frac{\theta}{2} \right\rangle (c_{i,ap}^+ c_{j,p} + c_{i,p}^+ c_{j,ap}) \right] \\ + t_{\text{Fe-Mo}} \sum_i d_i^+ \left[c_{i,p} + \left\langle \cos \frac{\theta}{2} \right\rangle (c_{i-x,p} + c_{i-x-y,p} + c_{i-y,p}) - \left\langle \sin \frac{\theta}{2} \right\rangle (c_{i-x,ap} + c_{i-x-y,ap} + c_{i-y,ap}) \right], \quad (2)$$

where $c_{i,p(ap)}$ destroys an electron in Mo at cell i with spin parallel (antiparallel) to the spin of the Fe core spin, and d_i destroys an electron in Fe at cell i , with the spin parallel to the core spin. H_{yz} and H_{zx} have identical form and give the same contribution to the total energy.

Close to the magnetic transition, we can write the hopping coefficients $\langle \cos(\theta/2) \rangle$ and $\langle \sin(\theta/2) \rangle$ as an expansion in m to second order

$$\left\langle \cos \frac{\theta}{2} \right\rangle \sim \frac{2}{3} + \frac{2}{5} m^2 \\ \left\langle \sin \frac{\theta}{2} \right\rangle \sim \frac{2}{3} - \frac{2}{5} m^2, \quad (3)$$

where we are following the same procedure as in Ref. 27,28 Using these expressions in the Hamiltonian in Eq. (2), and taking into account that there are three equivalent 2-dimensional bands, the kinetic energy can be calculated as a function of m : $E_{\text{KE}} = E_{\text{KE}}^0 + \chi m^2$. Knowing that the entropy of the spin system is

$$TS = \frac{1}{\beta} \left(\log \left(2 \frac{\sinh(\beta h)}{\beta h} \right) + m \beta h \right), \quad (4)$$

where h is an external magnetic field and $\beta = k_B T_C$, and that $\partial^2 F / \partial m^2 = 0$, we get $T_C = 2/3 [\partial E_{\text{KE}} / \partial (m^2)]$ [27, 29] (see Appendix A).

Numerical results for T_C with parameters $J - \Delta = 0.3$ eV, $t_{\text{Mo-Mo}} = 0.15$ eV, and $t_{\text{Fe-Mo}} = 0.3$ eV are shown

in Fig. 2. These parameters are consistent with ab-initio calculations⁶ and similar to the ones used in previous theoretical works on this model.^{24,25} $J + \Delta$ is considered to be infinite as the transitions to the Fe spin level parallel to the localized spin involve very large energies.²⁴ The results are in agreement with Monte-Carlo²⁵ and dynamical mean-field theory²⁴ calculations but in disagreement with experiments. In general, the calculated T_C is lower than that measured in experiments and shows a maximum around $c \sim 1$, while it is suppressed for larger electron densities $c \sim 2$. This behavior persists for a wide range of parameters ($0 < t_{\text{Mo-Mo}} < 0.25$ eV, $0 < t_{\text{Fe-Mo}} < 0.5$ eV, and $-1.5\text{eV} < J - \Delta < 1.5\text{eV}$).

The maximum of T_C around $c = 1$ and its suppression around $c = 2$ is related to the form of the density of states. Around $c = 1$ there is a maximum on the DOS and, close to $c = 2$ both parallel and anti-parallel spin bands from Mo are filled. The effect of this filling is more easily understood by introducing an effective Heisenberg model.

A. Effective Heisenberg model

To analyze the source of the discrepancy between theory and experiment the energy is written as a function

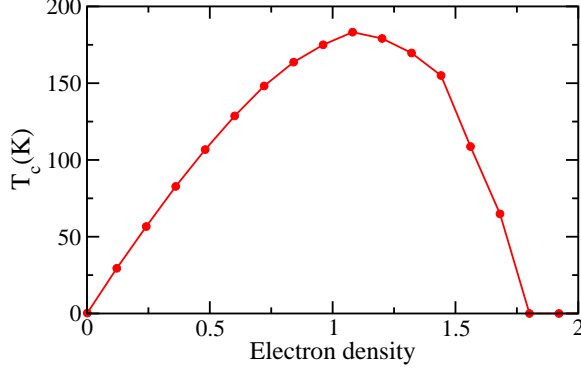


FIG. 2: (color online) T_C versus electron density c for a particular set of parameters $J - \Delta = 0.3\text{eV}$, $t_{\text{Mo-Mo}} = 0.15\text{eV}$, and $t_{\text{Fe-Mo}} = 0.3\text{eV}$. For all the range of parameters studied, there is a peak in T_C around $c \sim 1$ and $T_C = 0$ at $c \sim 2$.

of the relative angle between neighboring spins

$$\Delta E = - \sum_{\langle i,j \rangle} \left(J_C^{\text{Fe-Mo}} \cos \frac{\theta_{ij}}{2} + J_C^{\text{Mo-Mo}} \cos \frac{\theta_{ij}}{2} + J_S^{\text{Fe-Mo}} \sin \frac{\theta_{ij}}{2} + J_S^{\text{Mo-Mo}} \sin \frac{\theta_{ij}}{2} \right), \quad (5)$$

where the J 's are the expectation values of the operator pairs in Eq. (2). In the $m \rightarrow 0$ limit, Eq. (5) is an effective Heisenberg model,

$$\Delta E^{\text{Heis}} = - \frac{1}{2\sqrt{2}} \sum_{\langle i,j \rangle} J_{\text{eff}} \cos \theta_{ij}, \quad (6)$$

with

$$J_{\text{eff}} = J_C^{\text{Fe-Mo}} + J_C^{\text{Mo-Mo}} - J_S^{\text{Fe-Mo}} - J_S^{\text{Mo-Mo}}. \quad (7)$$

Therefore, this effective Heisenberg model has competing ferromagnetic (J_C 's) and antiferromagnetic (J_S 's) terms. In Fig. 3(a) the values of the four different couplings are plotted as a function of electron density. As shown in Fig. 3(b), the total coupling J_{eff} is antiferromagnetic for large values of electron density. The electron density at which J_{eff} becomes zero does not change significantly within the range of the tight-binding parameters used. Therefore, we cannot expect to override the suppression of T_C within this model. The competition between the ferromagnetic and antiferromagnetic channels can lead to phase separation,²⁵ due to the fact that J_{eff} (and, consequently, T_C) depend strongly on the electron density.²⁹

The ferromagnetic and antiferromagnetic channels are degenerate in energy since Mo is paramagnetic and both parallel and antiparallel states are equally populated.

B. Coulomb interaction

It is clear from the previous section that the degeneracy of ferromagnetic and antiferromagnetic channels needs to

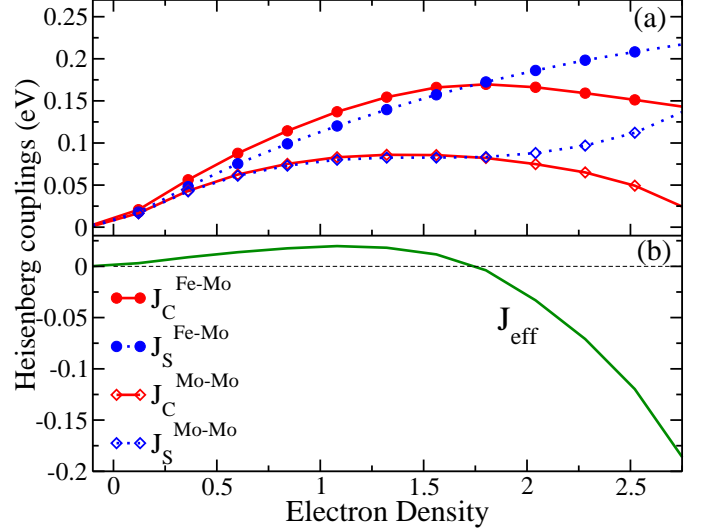


FIG. 3: (color online) (a) Heisenberg coupling values for the ferromagnetic (solid) and antiferromagnetic (dashed) channels. The antiferromagnetic coupling gets stronger for large electron density $c > 1.5$. (b) The total coupling J_{eff} as defined in Eq. (7).

be broken to obtain agreement with experimental results. Therefore, double occupancy of a site must be penalized which is, of course, expected in the presence of Coulomb interaction induced on-site electron correlations (so far neglected in the theory). This can be done with an intraband Hubbard term of the form

$$H_U = U \sum_i n_{i\uparrow} n_{i\downarrow}. \quad (8)$$

In Fig. 4, T_C is plotted for different values of U . Using relatively small values for U ($U \ll W \sim 8t$), we observe that T_C is strongly enhanced and the position of the maximum is shifted up from $c \sim 1$, consistent with experiment.

IV. MEAN FIELD APPROXIMATION. NON DISPERSIVE MO BANDS.

If we neglect the direct hopping between the Mo or Re orbitals, the connection between the model studied here and the double exchange model used in the description of the manganites becomes transparent. The Mo, Re orbitals can be replaced by an energy dependent direct Fe-Fe hopping, and a correction to the energy of the Fe orbitals. These quantities are:

$$\begin{aligned} \epsilon_{\text{Fe}} &= \epsilon_{\text{Fe}}^0 - \frac{t_{\text{Fe-Mo}}^2}{\omega - (J - \Delta)} \\ t_{\text{Fe-Fe}} &= \frac{t_{\text{Fe-Mo}}^2 \cos(\theta_{ij}/2)}{\omega - (J - \Delta)}. \end{aligned} \quad (9)$$

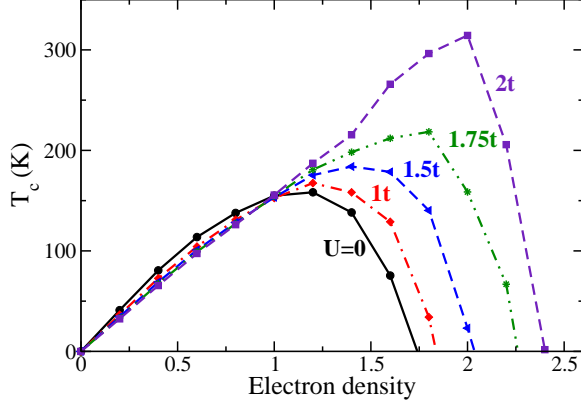


FIG. 4: (color online) T_C versus electron density c for different values of the Hubbard U . $J - \Delta = 0.3$ eV, $t_{\text{Mo-Mo}} = 0.15$ eV, and $t_{\text{Fe-Mo}} = 0.3$ eV. Moderate values of Coulomb repulsion U produce a large increase in critical temperature and its suppression is shifted to higher electron density.

When the separation between the Fe and Mo levels, $J - \Delta$, is large compared to the effective hybridization of the Fe levels, namely,

$$|J - \Delta| \ll \frac{t_{\text{Fe-Mo}}^2}{|J - \Delta|}, \quad (10)$$

the model reduces to an effective double exchange model,²⁷ with hopping integral:

$$t_{\text{eff}} = \frac{t_{\text{Fe-Mo}}^2 \cos(\theta_{ij}/2)}{|J - \Delta|}. \quad (11)$$

A mean field solution to the problem can be obtained by making the substitution:

$$\left\langle \cos\left(\frac{\theta_{ij}}{2}\right) \right\rangle = \sqrt{\frac{1 + \langle m \rangle^2}{2}}, \quad (12)$$

where m is the temperature dependent magnetization of the Fe ions.

Keeping the full energy dependence of the tight binding parameters in Eq. (9), one finds a self consistent solution for the band structure, which can be written as a quadratic equation for the band energies, $\epsilon_{k_x k_y}^\pm$. This equation can be solved, and we obtain:

$$\begin{aligned} \epsilon_{k_x k_y}^\pm &= J + \frac{\Delta - J}{2} \pm \sqrt{\frac{(\Delta - J)^2}{4} + 4t_{\text{Fe-Mo}}^2 \left\{ 1 + \sqrt{\frac{1 + \langle m \rangle^2}{2}} \left[-1 + (\cos(k_x) + \cos(k_y))^2 \right] \right\}}, \\ \epsilon_{k_x k_y}^0 &= \Delta. \end{aligned} \quad (13)$$

These equations give the exact solution of the model at zero temperature ($m = 1$), and they should describe qualitatively the changes in the electronic structure induced by the magnetic fluctuations. Note that the absence of direct hopping between Mo orbitals leads to a dispersionless band which has only weight at the Mo sites.

From the knowledge of the dependence of the electronic bands as function of the magnetization, one can calculate the electronic contribution to the free energy, and obtain the value of the Curie temperature, as discussed in Appendix A. We find:

$$T_C = \frac{2}{3} \frac{\partial^2 E_{\text{KE}}}{\partial \langle m \rangle^2} = \int \int_{\epsilon_k \leq \epsilon_F} d^2 k \sum_i \frac{\pm t_{\text{Fe-Mo}}^2 \left\{ [\cos(k_x) + \cos(k_y)]^2 - 1 \right\}}{\sqrt{\frac{(\Delta - J)^2}{8} + 2t_{\text{Fe-Mo}}^2 \left\{ 1 + \sqrt{\frac{1}{2}} \left[-1 + (\cos(k_x) + \cos(k_y))^2 \right] \right\}}}. \quad (14)$$

The main drawback of this approximation is that it does not allow to estimate the contribution of the direct hopping between Mo orbitals, $t_{\text{Mo-Mo}}$, which is expected to be comparable to $t_{\text{Fe-Mo}}$. These terms tend to reduce

the dependence of the electronic energy on the magnetization of the Fe sites, lowering the value of T_C . The qualitative dependence of T_C on band filling obtained in this approximation is, however, similar to the one con-

sidered in Sec. III, with $T_C \rightarrow 0$ for electronic densities $c \approx 2$. This fact can be explained, qualitatively, by noting that the value of T_C in the effective double exchange model derived here tends to have a maximum when the band is half filled. Because of the triple degeneracy of the Mo orbitals, the corresponding density is $c = 1.5$.

V. CONCLUSION

We have developed a mean field theory for double perovskites, e.g. $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$, within a minimal effective model (Fig. 1) including the strong Hund's coupling on the Fe sites and the various contributions to the kinetic energy of electron hopping between t_{2g} orbitals through the Mo sites. Ferromagnetism arises in the system due to constraints imposed on the hopping kinetic energy, rather than due to Fe-Fe superexchange. Our simple mean field theory reproduces the earlier theoretical results obtained with dynamical mean field approximation²⁴ and direct Monte Carlo simulations.²⁵ Our theory gives a reasonable semi-quantitative description of the observed Curie temperature in the double perovskites for the 'undoped' $x = 0$ system where the carrier density $c = 1$ (per unit cell). But, for the doped double perovskites ($x \neq 0$) our mean field theory, along with the existing theories of Refs. 24 and 25, predicts a decreasing T_C with increasing x (with $c = 1 + x$ for electron doping and $c = 1 - x$ for hole doping), which disagrees with experimental observations. The experimental finding is that T_C increases with doping whereas the theory finds a maximum around $c \approx 1$ (i.e. $x = 0$).

We suggest, based in our mean-field formalism, that the experimental observation of increasing T_C with doping may be an electron correlation effect which opposes double occupancy of sites due to intraband Coulomb repulsion. By introducing a simple Hubbard-U type intraband correlation term, we qualitatively reproduce the experimental trend of increasing Curie temperature with increasing doping. In addition, the introduction of the Hubbard-U term also enhances the T_C itself bringing theory and experiment into better quantitative agreement. We therefore believe that strong correlation effects are an inherent property of double perovskites.

Finally, we discuss the possible connection between double perovskites (DP) and diluted magnetic semiconductors (DMS), e.g. $\text{Ga}_{1-x}\text{Mn}_x\text{As}$, from the perspective of magnetism. At first, one notices some superficial similarities between DP and DMS materials: both have optimal T_C of the order of a few hundreds of Kelvin (although the highest reported T_C in GaMnAs is around 200K, substantially below the room temperature T_C 's routinely seen in DP materials); both manifest T_C 's increasing with doping, thereby indicating a role for carrier mediated ferromagnetism. There are, however, important differences between DMS and DP magnetic properties. In DMS, $T_C = 0$ for $x = 0$ since Mn atoms serve the dual roles of dopants (providing the carriers, which

are holes for $\text{Ga}_{1-x}\text{Mn}_x\text{As}$) and magnetic moments (i.e. the long range ferromagnetic order arises from the order of the local Mn moments), and therefore ferromagnetism vanishes in the absence of Mn. Thus the $x = 0$ situation in DMS is qualitatively similar to the $x = 1$ DP situation. The common model^{16,17} adopted in the literature to understand DMS ferromagnetism is a carrier-mediated RKKY-Zener indirect exchange coupling between the Mn moments, with the mean-field DMS T_C given by $T_C \sim |J_{pd}|^2 x n^{1/3}$, where J_{pd} is the local 'pd' exchange coupling between the Mn d-level and the p-type holes (with density n) in the valence band of GaAs. This RKKY-Zener type DMS mean-field theory is obviously completely inapplicable to the DP materials as it would predict an absurd DP T_C of $10^5 - 10^6\text{K}$ or larger (since both the magnetic moment density and the carrier density are substantially higher in DP materials than in DMS materials). We have developed the appropriate DP mean-field theory in this paper with a reasonable $T_C \sim 10^2 - 10^3\text{K}$.

It has, in fact, been suggested in the literature³⁰ that the DMS systems may actually be closer to the non-perturbative double-exchange limit than the perturbative RKKY limit. In such case, the DMS and the DP systems are more similar in nature (and they are both then closer to manganites, which are the quintessential double-exchange materials^{31,32}). But, in this limit, increasing doping should invariably lead to the eventual suppression of T_C , as we find in the theory developed in this paper. An important difference between DP and DMS materials is, however, the fact that the DMS systems lose their ferromagnetism (i.e. T_C becomes zero) for large values ($x \sim 0.1$) of Mn concentration. This also sharply distinguishes the DMS and the DP materials. A natural question, based on our argument in favor of the important role of a Hubbard type U-term in the DP materials is whether such electron correlation effects are also important in DMS materials. The answer to this question is not obvious at this stage. One possibility is that correlation effects are completely negligible in the DMS systems since the effective carrier density is extremely low ($n \sim 10^{19} - 10^{20} \text{ cm}^{-3}$ in DMS compared with $10^{22} - 10^{23} \text{ cm}^{-3}$ in DP materials), making the physics of double occupancy irrelevant. Much more work will obviously be needed to further understand the relationships and the differences in the magnetic properties and mechanisms for various 'oxide-type' magnetic materials such as manganites, double perovskites, diluted magnetic semiconductors, magnetically doped magnetic oxides (e.g. $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$), and even systems such as $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ where correlation effects are thought to play an important role.

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APPENDIX A: MEAN FIELD EXPRESSION FOR THE CURIE TEMPERATURE

The Free Energy of a system of classical spins of magnitude unity in an external magnetic field h is

$$F = -\frac{1}{\beta} \log \left(2 \frac{\sinh(\beta h)}{\beta h} \right), \quad (\text{A1})$$

from where the magnetization can be calculated as

$$m \equiv \langle m \rangle = -\frac{\partial F}{\partial h} = \frac{1}{\tanh(\beta h)} - \frac{1}{\beta h}. \quad (\text{A2})$$

The entropy of the spin system is then

$$-TS = F - mh = \frac{1}{\beta} \left(-\log \left(2 \frac{\sinh(\beta h)}{\beta h} \right) - m\beta h \right). \quad (\text{A3})$$

The total energy of the system, assuming the electrons are at zero temperature and neglecting direct interactions between Fe spins, can be written

$$F^{\text{total}} = \chi m^2 - TS = \chi m^2 - \frac{1}{\beta} \left(\log \left(2 \frac{\sinh(\beta h)}{\beta h} \right) + m\beta h \right), \quad (\text{A4})$$

where χm^2 is the kinetic energy of the conduction electrons.

To obtain h , we minimize the total free energy with respect to h , $\partial F^{\text{total}}/\partial h = 0$. In the limit of small h

$$\frac{\sinh(\beta h)}{\beta h} \equiv 1 + \frac{(\beta h)^2}{6} \\ \log \left(2 \frac{\sinh(\beta h)}{\beta h} \right) \simeq \log(2) + \frac{(\beta h)^2}{6}. \quad (\text{A5})$$

In this limit, the minimization condition gives $\beta h = -3m$, and the free energy gets the form

$$F^{\text{total}} = -\frac{1}{\beta} \log(2) + m^2 \left(\chi + \frac{3}{2} k_B T \right). \quad (\text{A6})$$

Therefore, the Curie temperature is²⁹

$$k_B T_C = -\frac{2}{3} \chi \quad (\text{A7})$$

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